## Chemical Occurrences - November, 1997

### Class 1:

<u>INEEL</u> - Unprotected employee burned by sulfuric acid spray

#### Class 2:

ETEC - Employee eye irritation due to NaO/NaOH aerosol release

Savannah River - Workers exposed to nitric acid fumes during transfer activities

#### Other Observations:

Pressurized drums \*\* USQDs: Fire Protection \*\* Explosives at LLNL

A search of ORPS for occurrences having chemical safety relevance conducted for the month of November 1997 produced 29 reports representing potential chemical safety concerns. These occurrences are listed in <a href="Attachment 1">Attachment 1</a>. There were five occurrences categorized as "Unusual" with the remainder identified as "Off-normal". The Office of Environmental Management (EM) was Cognizant Secretarial Office (CSO) for 19 occurrences; Defense Programs (DP) reported six; Nuclear Energy (NE) had three, and Energy Research (ER) one. The CSO designation may change after the distribution of this monthly memorandum, and this change will be reflected in Quarterly and Annual Reviews.

There was one Class 1 and two Class 2 occurrences reported during November. There were 12 Class 3 occurrences. (Class definitions) Among the Class 3 occurrences, in addition to those noted previously, was a hydrogen accumulation concern at the Hanford tank farms due to minimum purge flow not being verified. At PNNL, a gas heater was found to be leaking (odor detected).

# **Summaries of Class 1 and Class 2 Occurrences:**

Acid Sprays onto Unprotected Employee (NE): (ID--LITC-ATR-1997-0025) On November 20, at the INEEL, an operator was sprayed with a foam-like sulfuric acid spray while disconnecting an air hose to an air sparge line of a bulk acid storage tank. The tank was being cleaned at the time of this event and was empty. Acid had accumulated in the air line over a period of time. The operator was treated at the dispensary where it was determined that he had been burned on the neck, ears, and arms. Pre-job planners did not recognize that the airline hose connection should have been included inside the boundaries ("safety envelope") of the safe work zone. Since the operator was working outside the posted area, he did not wear personal protective equipment. The facility manager's remarks in the occurrence report are worth noting: "Despite extensive safety preplanning, this hazard was not recognized and it was fortuitous that the operator was not more seriously injured. It is likely that more conservative requirements for wearing personal protective equipment adjacent to the acid tank and associated piping will be implemented for all evolutions as a result of this event." More information regarding this occurrence is reported in OEWS 97-49.

**Nitric Acid Release - Odors Detected (EM):** (SR--WSRC-SEPGEN-1997-0004) On November 2, at Savannah River, an operator completed a transfer into a nitric acid tank; the operator smelled acid fumes and saw acid spreading from an area around an adjacent sink. Approximately five hours later, personnel noted that acid was leaking from an open flange on the acid drain header that connects to the transfer

line. The valve in this line was locked-out, but indications are that the lockout was inadequately established and did not adequately establish and address system boundaries. Industrial Hygiene (IH) dispatched an inspector to take acid vapor concentration readings in the affected areas. Acid vapor concentrations at the immediate area of the spill was 30 parts per million (ppm) and 5 ppm in the area surrounding the nitric acid accumulation. Acid vapor concentrations in HB-Line did not exceed IDLH (Immediately Dangerous to Life and Health) threshold levels (45 ppm). It is, however, stated in the occurrence report that "initial IH surveys showed 45 ppm at the spill site..."

Also, at Savannah River (SR--WSRC-FCAN-1997-0052), on November 6, a line break was conducted to support removal of an automatic inlet valve. Approximately 3 gallons of nitric acid drained from the piping into prepositioned buckets containing soda ash. The resultant nitric acid fumes exceeded the limit of 5 ppm limit as established in the job preplan meeting. The maximum airborne concentration recorded was 10 ppm. IH responded to survey and evaluate fume levels in the facility. Potentially affected personnel were sent to medical for evaluation.

Employee Eye Irritation - Aerosol Release (EM): (SAN--ETEC-GENL-1997-0002) On November 5, at ETEC, there were intermittent releases (over a 3-minute period) of sodium reaction products (NaOH and NaO) that occurred during a tank cleaning operation. Localized pockets of NaOH-water solution form over caustic within the tank and occasionally react with sodium resulting in the reaction products venting through the exhaust system. The operating engineer observed the reaction product release, and visually surveyed the general area outside the controlled area for the presence of personnel. The engineer observed delivery driver and requested that he get inside his vehicle and move out of the general vicinity. Later, the driver complained of eye irritation. He was taken to the local hospital where he was examined, his eyes washed, and he was released. He returned to work the next day following a second examination of his eyes where it was concluded by the physician that no further treatment was required.

There were two occurrences involving the generation or potential generation of hydrogen gas in waste storage drums: ALO-LA-LANL-WASTEMGT-1997-0005 and SR--WSRC-SLDHZD-1997-0019. Both occurrences express concerns about hydrogen concentration exceeding the Lower Flammability (Explosive) Limit (LFL = 4% in air). At Los Alamos, a USQ was identified: 12% of 600 drums exceeded LFL as opposed to 1% as per the Safety Analysis Report. At Savannah River, drum purge and lid ventilation were determined to be inadequate to obtain and maintain hydrogen concentration below LFL.

Two additional occurrences discovered in November involved potential USQs: CH-AA-ANLE-ANLEEMO-1997-0007 and ORO--LMES-Y12NUCLEAR-1997-0048. Both of these occurrences involved fire protection concerns. At ANL, the storage of flammable mixed waste was seen as an unanalyzed initiator of a possible explosion in a waste storage facility. At Y-12, identified issues, related to the storage of lithium compounds, involved both the duration of any fire and the amount of combustion products that could leak outside the storage building.

There were also two occurrences at LLNL (SAN--LLNL-1997-0066 and -0067) involving explosives. In one, it was discovered that S-300 explosive propellant was degraded with "unacceptably low stabilizer content." All nitrate ester explosives were to be tested for this degradation. In the second, perchlorates (shock-sensitive crystals) were discovered in a ventilation system not approved for containing perchlorates.

Additional information regarding these occurrences and others will be discussed in an upcoming Quarterly Review; some are currently summarized on this website. As occurrence reports are finalized, lessons learned will be communicated.

This report approved by

# Rama Sastry Office of Field Support

#### Note:

A version of this report is distributed via e-mail either as a WordPerfect or a text file. Please contact **John Usher** (516-344-2096, Fax: 516-344-3957, E-mail: usher@bnl.gov) at Brookhaven National Laboratory to be placed on e-mail distribution. If you want to receive hardcopy, please contact John Usher who will make every effort to accommodate you.

Please feel free to use the other resources available on the DOE Chemical Safety Program homepage. The Internet address is <a href="http://tis-hq.eh.doe.gov/web/chem\_safety/">http://tis-hq.eh.doe.gov/web/chem\_safety/</a>.